

THE SEPARATION OF MINERAL MATTER FROM PITTSBURGH COAL BY WET MILLING

Douglas V. Keller, Jr.

Otisca Industries, Ltd.
P. O. Box 127, Salina Station
Syracuse, New York 13208

Introduction

The term "inherent mineral matter, or ash" is a commonly used phrase in the coal literature (1). The phrase refers to that fraction of the mineral matter bound organically to the carbonaceous structure of the coal and estimates of its content suggest that it is in the range of two weight percent of the whole mineral matter (1). Common classical physical separation schemes such as differential specific gravity separations or froth flotation which are directed at demineralizing the coal never approach that lower limit. For example, at the outset of this investigation one could receive a raw Pittsburgh seam coal at 30 weight percent ash and through careful float-sink processes reduce that ash content into the range of four to five weight percent. Practically reducing that ash content, however, to below three weight percent with a reasonable yield was quite unlikely (2). One consequence of the large weight fraction differential between the practical limit of demineralization, and if you like, the true "inherent" limit of demineralization was a total lack of understanding as to whether or not that mineral fraction could indeed be extracted by physical means. With this as a basis, further questions could be raised as to whether or not that retained mineral matter was a true distinct mineral phase, or if so, could it be bound chemically along the interfaces to the coal structure rendering those particles inseparable. Most simply, in all cases one could ask the question does a separation of mineral matter from the coal take place in all cases when coal is fractured and to what extent, or limit, can the fracture process be utilized in the demineralization of coal.

A series of experiments was assigned to explore the extraction of mineral matter from coal in the size ranges below 0.25 mm. The raw coal samples were obtained from three different sources in the Pittsburgh seam which permitted a degree of comparison over a rather large geographic area. The results are interesting in that they allow a new perspective in the demineralization of coal.

Experimental

The Pittsburgh seam coals used in this investigation has a nominal analysis as illustrated in Table 1.

Lots of Pittsburgh seam coal in excess of 1000 pounds each were received from three different sources in Washington County: Mine (A) was located about 20 miles west of Pittsburgh; Mine (B) was located just south of Pittsburgh; and Mine (C) was located about 40 miles south of Pittsburgh. Representative samples from each source were obtained by ASTM procedures and subjected to the following processing.

A raw coal sample was reduced to 250 μ m x 0 by dry mechanical crushing in a hammermill and then ground in a laboratory sample mill.

The mechanically ground coal was then mixed with water to form a slurry with 30 weight percent solids and placed in a standard laboratory ball mill. All of ball milling variables were held constant except for the duration of milling which permitted a variation of the particle size distribution. In the event that chemicals were employed during the ball milling operation those chemicals were incorporated in an excess of the amount of the standard mill content.

The coal water slurry was removed from the mill, diluted with water to ten weight percent solids and the coal fraction removed utilizing the Otisica T-Process (2,3). Separations by the T-Process are unique in that agglomeration results in the recovery of virtually 100% of the carbonaceous material leaving a full dispersed mineral phase in the residue water. Many detailed investigations of this type have concluded that mineral matter recovered with the coal phase is included in the coal that is the ash content of the product coal represents only that mineral matter mechanically attached to or enveloped by the coal.

Analytical procedures for ash (high temperature, HT) and sulfur contents were conducted according to ASTM procedures. Low temperature ash procedures were conducted at 550°C in an oven with an adequate supply of oxygen. The difference in mineral matter morphology and chemistry between this technique and the low temperature ashing method described by Gluskoter (3), can be anticipated from the paper by Mitchell and Gluskoter (4). Principally the higher temperature ashing process will convert pyrite to hematite and kaolinite to metakaolinite. Between 30% and 50% of the mineral matter in the Pittsburgh coal is considered to be kaolinite (5), and in this investigation we presumed that the 550°C ashing procedure did not significantly alter the particle size distribution of the original kaolinite particles.

A Micromeritics 5500L unit was used to obtain the particle size distribution data for this investigation. Data from the Micromeritics unit using a one μm mode sample was compared with the data developed by the manufacturer from a Coulter Counter on the same sample to within ten percent. Even with this in hand there was no attempt to characterize the particles on an absolute basis. The observed area percent data from the Micromeritics unit was transposed to a mass percent base at data points y (in μm) for all of the points $y = 2^x$ where $x = n + 0.5$ and $n = -3, -2.5, \dots, 0, \dots, +7, +7.5$. The data point at y represents that mass fraction of material lying in the size range $x \pm 0.25 \mu\text{m}$. Thus a summation of all of the data points represents the mass fraction of ash, or product coal, as the case might be.

The following particle size distribution data are given as a log distribution in particle diameter (μm) where the mass points are interconnected for convenience of comparison at the expense of rigor. Typical distributions are bell-shaped where the mode is defined as the particle diameter at that point of half width of the curve at the half height of the maximum. The Micromeritic unit is based on a Stokes' Law settling to the particles where one must choose an average specific gravity of particles under investigation before the data are recorded. In those cases where low temperature ash particles were investigated, the iron minerals with a density larger than 4 gms/cc were separated from the clay minerals with densities less than 3 gms/cc, the distributions measured individually and then the size distributions were recombined mathematically. The product coals demonstrated a very narrow specific gravity distribution in the range of 1.33.

Results and Discussion

Figure 1 illustrates the particles size distribution of the mineral matter that results from the low temperature ashing of three 5 cm cubes of bright coal that were hand-picked from the various samples. The ash contents were in the range of five weight percent. It is of interest to note that band of mineral matter particles that lie in the particle diameter range between one and 50 μm with a mode between four and eight μm . The particle size distribution data from the low temperature ashing of the 5 cm cubes of coal show that raw coal from each source has a unique "fingerprint" of mineral matter particles distributed in the particle size range below 0.25 mm.

Investigations of many other coal seams and coals within a particular seam indicate that indeed the mineral matter distribution varies widely both in shape and magnitude and as such cannot be anticipated from other coal properties. The mineral matter distribution is a fundamental property of that coal which is an uncontrolled natural variable in the extraction of mineral matter.

In order to demonstrate that the 5 cm cube was constituted of an accumulation of much smaller unit volumes each of which represented the whole coal in mineral matter particle size distribution a study of a series of size classified particles was undertaken. For example, if raw coal (C) were ground to 250 μm x 0, and then separated with standard sieves into the size fraction 53 x 44 μm , we would be afforded a dry mixture of raw coal particles and mineral particles with an average size of 48 ± 4 μm . Figure 2 illustrates the particle size distribution of the low temperature ash product of the product coal after the free mineral matter particles were removed. The free mineral matter particles in that size range must have evolved from larger coal particles. Again we have the characteristic curve very similar to the curve shown in Figure 1(C). In fact, that portion of the curve that lies below 3 μm can most usually be superimposed on other curves obtained in a similar manner from the other size fractions of coal (C). Providing, that is, that the coal particle diameters are larger than 10 μm .

The conclusion of that study indicated that product coal particles larger in diameter than the band of microparticles seemed to contain the whole particle distribution of the small microparticles of mineral matter. That is, there appeared to be a relatively homogenous distribution of particles throughout limited in top size by the largest particle in the test. To explore that aspect in more depth, a raw coal was wet milled to smaller sizes.

When a raw coal is wet ball-milled for a sufficient time to produce a slurry with a particle diameter mode in the range of 4 μm there results two forms of mineral matter: That fractured away from the coal and that which is still enveloped in the coal particles. Figure 3 illustrates a typical particle size distribution for the separated product coal as compared to the separated free mineral matter (90 weight percent ash) from one milling test. The separated mineral matter is clearly smaller in diameter than the coal which is probably due to its more brittle properties. Note that in Figures 3 and 4 an integration of the curves will yield 100% of the mineral matter (or ash) under consideration rather than the ash content of the coal as was the case in Figures 1 and 2.

When the product coal shown in Figure 3 was subjected to low temperature ashing as described above and that product subjected to particle size analysis, a curve as is illustrated in Figure 4 results. Clearly the enveloped mineral matter in the product coal particles is considerably smaller in diameter than the coal particles from which they came and as such are not released for separation.

Two very important points are illustrated in Figures 1-4: Firstly, it appears that as coal fracture takes place in this system, mineral matter particles are ejected from the fractured coal system and most without attached coal. Coal attached to mineral matter is recovered as product coal. The implication is that the coal-mineral matter interfaces are not chemically bound. If those interfaces were chemically bound one would observe mineral matter rejection with a large increase in the sub-micron particle population in the released mineral matter, cf. Figure 3, as well as that in the low temperature ash of the product coal. The latter is not observed as is illustrated below.

Secondly, given the low temperature ash distribution of the raw coal and a knowledge of the raw coal particle size distribution after wet milling, we are in a position to predict the ash content of the product coal. Consider Figure 5 where a hypothetical low temperature ash particle size distribution is superimposed on a T-Process product coal size distribution. The product coal particles with diameters lying between x and dx contain no mineral matter particles larger than dx as those particles were removed during the separation process. The mineral matter retained in the product coal particles is the cumulative mineral matter content represented by the low temperature ash curve. Since the mineral content given on the ordinate in Figure 5 is based on 100%, the ash content in each size range can be estimated by multiplying the mass fraction of that point by the total ash content in the raw coal sample, i.e. 250 m x 0, that was used to generate the low temperature ash curve.

A specific case is examined in Table 2 where the particle size distribution data from the low temperature ashing of a 5 cm cube of coal and 44-53 μ m coal was related to two product coal samples milled under different conditions all of which originated from the same source coal (C). The first column in Table 2 provides the average particle diameter points (y) at which the data were observed. A comparison of the low temperature ash data for the 5 cm cube, column 2, and for the 44-53 μ m coal, column 3, illustrate that the fracture of coal from a 5 cm cube to 48 μ m does not significantly disturb the mineral matter particles lying in the range of diameters below 6 μ m. Since a 4 μ m particle of product coal ought to have the complete mineral matter particle distribution smaller than 4 μ m enveloped in that particle, a cumulative ash fraction of the lesser particle diameter ash should be equivalent to the ash content within the 4 μ m particles, that is, 2.67 weight percent ash, cf. column 4 at 4 μ m.

A test of this relationship is afforded in column 5 where we observe the mass fraction of particles at various diameters of a product coal from a standard mill run with no chemicals added. The predicted ash content of the product coal is determined by a summation, over all particle diameters of the product of the ash content of each diameter cumulated by increasing diameter, (x) times the mass fraction of the product coal at that particular diameter (y). The predicted ash content for this case is 1.19 weight percent ash which can be compared to

the observed value using ASTM procedures of 1.12 weight percent ash. Following identical milling procedures, except for the addition of 20 pounds per ton ligninsulfonate, a dispersant, we obtain a much finer size distribution as is illustrated in column 6, Table 2. The predicted ash content in that case is 0.68 weight percent ash while the observed value was 0.91 weight percent ash. The large discrepancy in the finer coal case was probably due to imperfect separation procedures that were caused by the presence of the dispersant. The ability to predict ash contents using this procedure has been applied to several different coals from different seams and the same seam with results usually within ten percent. A careful examination of these data lends credence to the observation that for the most part the mineral matter included in coal to the micron particle size range is indeed a distinct separable phase capable of physical separation by fracture.

The extent to which milling can be carried out and still attain effective demineralization is to a degree limited by our knowledge of milling. Coal B was reduced in ash into the range of 0.5 weight percent, however, that limit appeared to be a function of milling phenomena rather than fracture phenomena. Clearly, according to the analysis shown in column 5 of Table 2 and the subsequent discussion, one might expect a monotonic decrease in product coal ash content with particle size distribution mode to zero mineral matter which has not been observed. What was not anticipated was the observation that that relation appeared to be insensitive to what might be considered as rather severe changes in the chemical environment during the milling process even though some of the chemical additives made significant changes in the milling efficiency, i.e., specific area increase per unit input energy. Consider the effect of three chemical additives: calcium hydroxide, sodium ligninsulfonate, and sodium sulfosuccinate, as compared to the case of no additives on the particle size distribution of the product coal from a standard mill run shown in Figure 6 where all conditions were identical. Clearly, there were no obvious effects. In the next series, shown in Figure 7, we investigated the additives ammonium hydroxide, sodium hydroxide, and a higher concentration of sodium ligninsulfonate. Clearly, a dynamic difference in specific surface area per unit input energy was observed. The explanation of the differences is beyond the scope of this paper, but what was interesting was the effect that the chemicals had on the fracture mechanism that effects the release of mineral matter. Figure 8 illustrates a plot of the ash content in the product coal versus the mode of the particle size distribution of the product coal. All of the tests utilizing chemical additives were milled under identical conditions utilized in the test which produced the "no additive" data with a 2 μ m mode. The three other "no additive" tests were milled for extended times to achieve smaller particle size distributions. The chemical additive calcium hydroxide when used at 20 pounds per ton is above the saturation limit and the solid particles have become imbedded in the coal structure, hence increasing the ash content of the product coal well removed from its anticipated location on the curve. A mild acid etch of that product coal to remove the calcium hydroxide allows recovery of its anticipated position in the scheme. Some of the chemical additives do alter the specific milling rate during the process, but that change does not alter the relationship between particle fracture and mineral matter released. Such lends support to the presumed model that the ultrafine mineral matter is to some degree homogeneously distributed and is only released with the fracture of the coal particle.

Conclusion

High ranked bituminous coals like those of the Pittsburgh seam contain a distribution of discrete mineral matter particles in the size range from 50 to 1 μm which can be released and physically separated from the coal by normal fracture mechanisms experienced in wet ball milling. Demineralization of coal by this mechanism appears to be a predictable process with an error in the range of 10 percent. The demineralization of Pittsburgh seam coal has been achieved to the range of 0.5 weight percent ash, a limit which appears to be controlled by the mechanics of the ball mill.

Acknowledgments

The author extends his sincere appreciation to W. Burry and D. S. Keller for their efforts in the development of the experimental procedures and data analysis.

References

1. Leonard, J. W., "Coal Preparation", Amer. Inst. Mining Met. Pet. Eng., Inc., New York (1979).
2. Keller, Jr., D. V., "Otisca T-Process, A New Coal Beneficiation Approach for the Preparation of Coal Slurries", Coal Gasification, Liquefaction, and Conversion to Electricity Conference, University of Pittsburgh, August 1982.
3. Keller, Jr., D.V., "Coal Refining by Physical Methods for the Preparation of Coal Slurries With Less Than 1 wt.% Ash", Fifth International Symposium on Coal Slurry for Combustion and Technology, Tampa, Florida, April 1983, U.S. DOE, Pittsburgh, p 269.
4. Gluskoter, H.L., Fuel, 44, 285 (1965).
5. Mitchell, R.S. and Gluskoter, H.L., Fuel, 55, 90 (1976).
6. O'Gorman, J.V. and Walker, P.L., "Mineral Matter and Trace Elements in U.S. Coals", U.S. Office of Coal Research, R& D Report No. 61, (1972).

TABLE 1

NOMINAL ANALYSIS OF PITTSBURGH SEAM COAL

	Weight Percent (Dry Basis)
Volatile Matter	35
Fixed Carbon	58
BTU/lb	14,200
Carbon	77.3
Hydrogen	5.2
Nitrogen	1.5
Chlorine	0.1
Sulfur	1.5
Oxygen (diff)	7.6
Ash	6.8

TABLE 2

PARTICLE SIZE DATA FOR LOW TEMPERATURE ASH PRODUCTS AND PRODUCT COALS

Data Point	Low Temperature Ash - Wt.%			Product Coal - Wt.%	
μm	5 cm Cube	44-53 μm	44-53 μm (Cumulative X)	Standard No Additives	Standard 20 pounds/ton Ligninsulfonate
(y)				(Y)	(Z)
0.35	0.03	0.06	0.06	0.08	0.14
0.50	0.06	0.1	0.16	0.05	0.08
0.71	0.19	0.18	0.34	0.085	0.13
1.00	0.35	0.28	0.62	0.13	0.20
1.41	0.49	0.38	1.0	0.2	0.14
2.0	0.67	0.52	1.52	0.18	0.10
2.83	0.63	0.60	2.12	0.145	0.05
4.0	0.66	0.55	2.67	0.06	0.03
5.66	0.66	0.55	3.22	0.04	0.01
No Additives		y = 5.66	$\Sigma (X_Y \times Y_Y) =$		
		y = 0.35	1.19 Wt.% Ash Predicted		
Ligninsulfonate		y = 5.66	1.12 Wt.% Ash Observed		
		y = 0.35	$\Sigma (X_Y \times Z_Y) =$		
			0.68 Wt.% Ash Predicted		
			0.91 Wt.% Ash Observed		

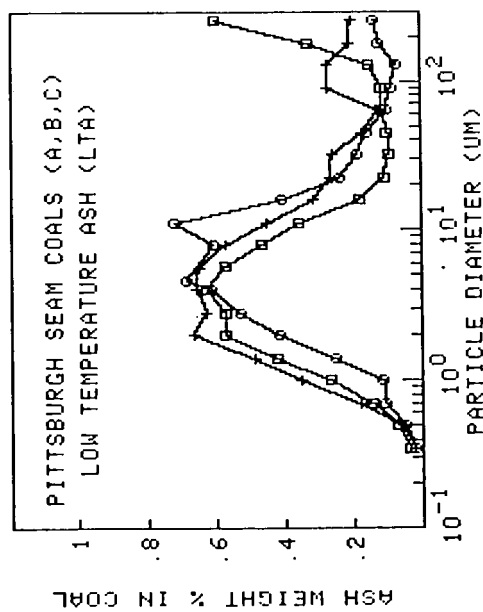


FIGURE 1: PARTICLE SIZE DISTRIBUTIONS OF THE LOW TEMPERATURE ASH PRODUCTS FROM THREE DIFFERENT 5 cm BLOCKS OF PITTSBURGH SEAM COAL: (*) Coal A; (□) Coal B; and (○) Coal C.

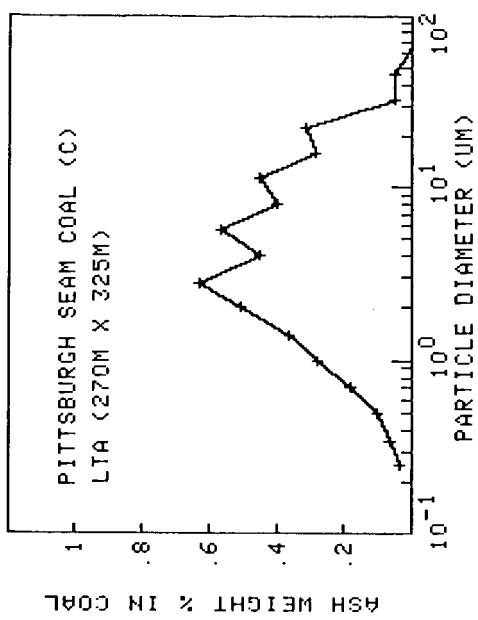


FIGURE 2: PARTICLE SIZE DISTRIBUTION OF THE LOW TEMPERATURE ASH PRODUCT OF A $48 \pm 4 \mu\text{m}$ PRODUCT COAL.

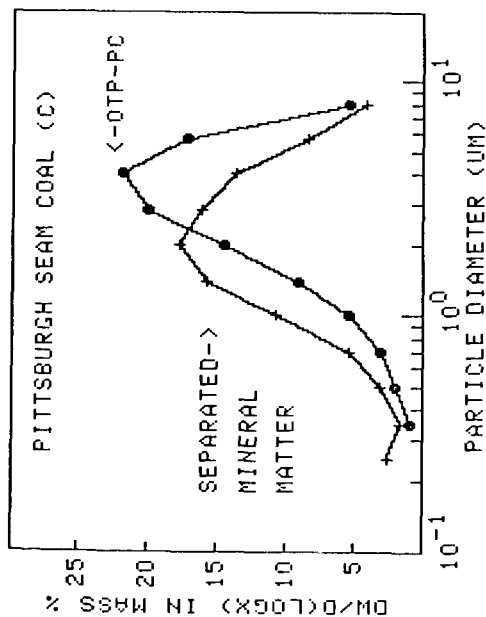


FIGURE 3: WHEN THE PRODUCTS OF WET MILLING 250 $\mu\text{m} \times 0$ PITTSBURGH COAL (C) ARE SEPARATED, TWO PRODUCTS EVOLVE: PRODUCT COAL AND SEPARATED MINERAL MATTER. THE PARTICLE SIZE DISTRIBUTIONS FOR EACH ARE ILLUSTRATED.

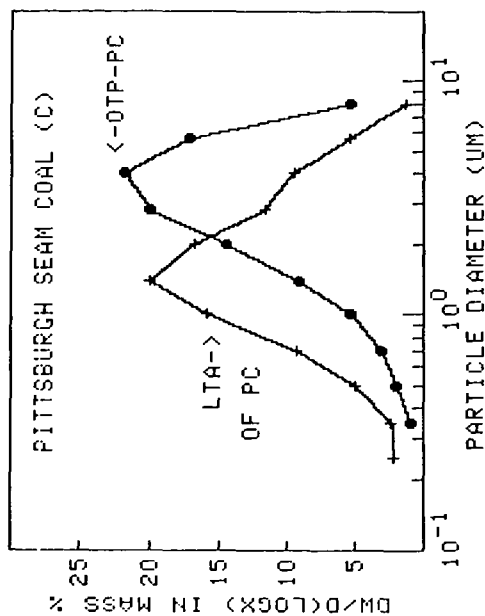


FIGURE 4: PARTICLE SIZE DISTRIBUTION OF THE LOW TEMPERATURE ASH PRODUCT FROM THE SAME PRODUCT COAL SAMPLE SHOWN IN FIGURE 3.

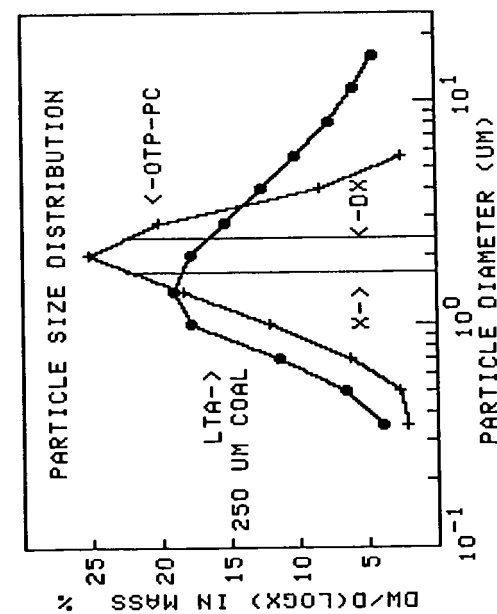


FIGURE 5: A HYPOTHETICAL PARTICLE SIZE DISTRIBUTION CURVE OF LOW TEMPERATURE ASH AND PRODUCT COAL.

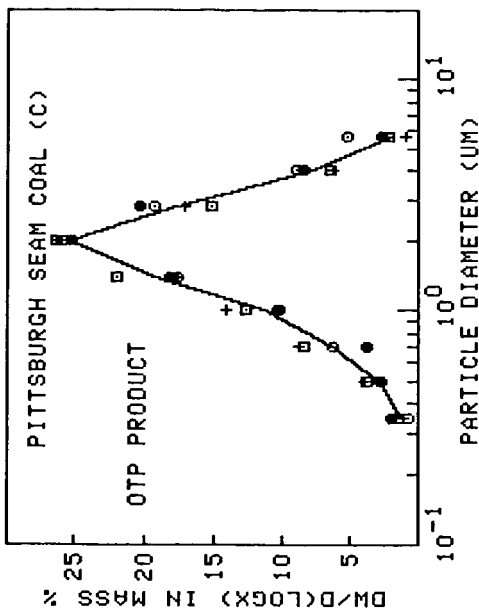


FIGURE 6: THE EFFECTS ON PRODUCT COAL PARTICLE SIZE DISTRIBUTION OF THREE CHEMICAL ADDITIVES WHILE MILLING AT CONSTANT CONDITIONS. (●) No Additives; (○) 2 lbs/ton Calcium Hydroxide; (□) 2 lbs/ton Sodium Lignosulfonate; and (+) 20 lbs/ton Sodium Sulfosuccinate.

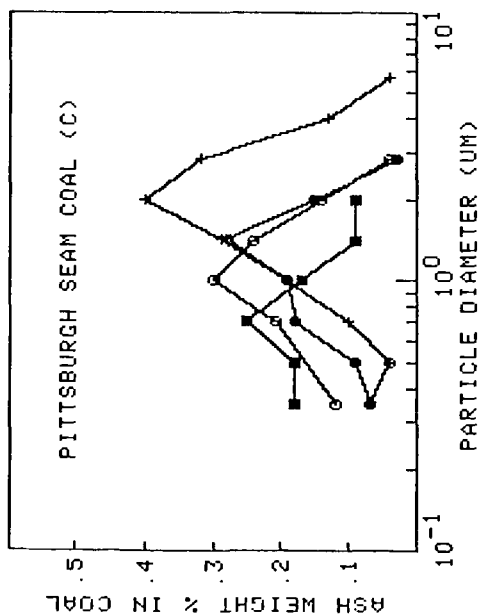


FIGURE 7: THE EFFECTS ON PRODUCT COAL PARTICLE SIZE DISTRIBUTION OF THREE CHEMICAL ADDITIVES WHILE MILLING AT CONSTANT CONDITIONS. (+) No Additives; (●) 36 lbs/ton Ammonium Hydroxide; (○) 7.9 lbs/ton Sodium Hydroxide; and (■) 20 lbs/ton Sodium Ligninsulfonate.

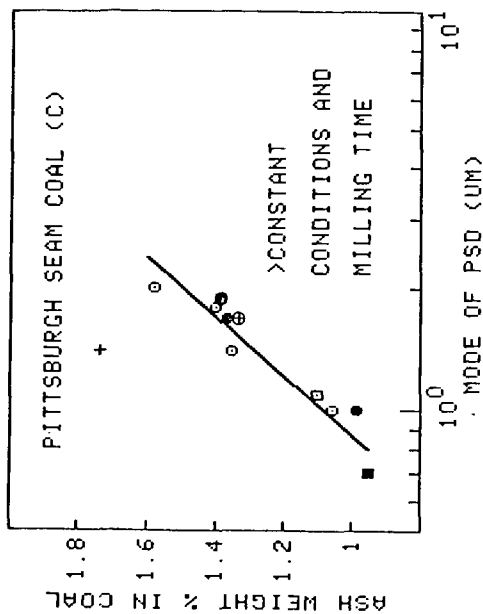


FIGURE 8: WEIGHT PERCENT ASH IN PRODUCT COAL VERSUS THE MODE OF THE PARTICLE SIZE DISTRIBUTION OF THE PRODUCT COAL. (○) No Additives; (●) 7.9 lbs/ton Sodium Hydroxide; (□) 20 lbs/ton Ammonium Hydroxide; (■) 20 lbs/ton Sodium Ligninsulfonate; (+) 20 lbs/ton Calcium Hydroxide; (●) 2 lbs/ton Sodium Ligninsulfonate; and (+) 20 lbs/ton Sodium Sulfosuccinate.